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NEW VARIATIONAL BOUNDS ON GENERALIZED POLARIZABILITIES.(U)
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NEW VARIATIONAL BOUNDS ON GENERALIZED POLARIZABILITIES

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ABSTRACT

New variational bounds are derived on the generalized polarizabilities of a quantum-mechanical system, for arbitrary complex frequencies $\zeta = \nu + i\omega$ and two different perturbations u and v. No power of the Hamiltonian h higher than h^2 is involved in the bounding functionals. For a certain range of ν-values, upper and lower bounding functionals are obtained which contain merely a single trial vector but also introduce an inverse operator like h^{-1}. This impractical feature can be avoided with a subsidiary variational principle, leading to bivariational upper and lower bounds. Explicit bivariational bounds are also derived which are valid for all values of ζ. Both theoretical and practical aspects of the bounds are discussed.

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Key Words: Polarizabilities, complex Hilbert space, bivariational bounds.

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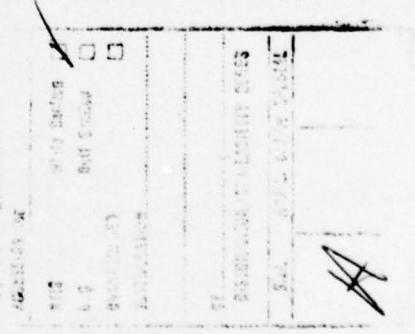

*On leave from Bradford University, England.

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NEW VARIATIONAL BOUNDS ON GENERALIZED POLARIZABILITIES†

Peter D. Robinson*

1. INTRODUCTION

Let a quantum-mechanical system be described by a self-adjoint Hamiltonian operator h in a complex Hilbert space H, and suppose that h possesses a complete set of orthonormal eigenvectors $\{\theta_k\}$ with corresponding energy eigenvalues $\{E_k\}$. If the system is in a state θ_n, its dynamic polarizability $\alpha(\zeta)$ at complex frequency $\zeta = \nu + i\omega$ associated with a perturbation u can be defined as

$$\alpha(\zeta) = 2 \text{ Real } \sum_{k\neq n} (E_k - E_n + \zeta)^{-1} \langle u\theta_n, \theta_k\rangle\langle\theta_k, u\theta_n\rangle , \tag{1.1}$$

the summation being over all states different from θ_n. The notation $\langle , \rangle$ denotes the complex inner product, so that for all Φ and Ψ in H and complex numbers s we have

$$\langle\Phi,\Psi\rangle = \overline{\langle\Psi,\Phi\rangle}, \quad \langle s\Phi,\Psi\rangle = \bar{s}\langle\Phi,\Psi\rangle, \quad \langle\Phi,s\Psi\rangle = s\langle\Phi,\Psi\rangle, \tag{1.2}$$

a bar denoting complex conjugate. Previous authors [see for example references 1-8 and 25-27] have presented bounding variational functionals on $\alpha(\nu)$ or $\alpha(i\omega)$, the dynamic polarizabilities when ζ is wholly real or wholly imaginary. Often there has been a restriction to real u and real θ_n. With $\omega\neq 0$, shortcomings of many of these bounding functionals have been the high powers of h involved, and a multiplicative factor of ω^{-1} which is unfortunate for small ω.

Expressions similar to that in (1.1), but with inner products $\langle v\theta_n, \theta_k\rangle\langle\theta_k, u\theta_n\rangle$ involving different perturbations u and v, define quantities

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arising for example in theories of optical rotatary power [9], and nuclear-magnetic shielding and chemical shifts [10,11]. Such more general expressions can also arise in double perturbation theory [12]. With generalizations such as this in mind, as well as the desirability of admitting arbitrary complex frequencies, perturbations and unperturbed states, we show how to derive upper and lower bounding variational functionals on the quantity

$$Z(f,g;\zeta) = 2\ \text{Real} \sum_{k\neq n} (E_k - E_n + \zeta)^{-1} \langle g,\theta_k\rangle\langle\theta_k,f\rangle \ . \tag{1.3}$$

No separate consideration is necessary for quantities defined as imaginary parts of summations like that in (1.3), for g can merely be replaced by $-ig$ if necessary. Without significant loss of generality, the arbitrary complex vectors f and g are taken as members of the reduced Hilbert space $H_n \subset H$, containing all vectors in H which are orthogonal to θ_n, i.e.

$$f,g \ \varepsilon \ H_n = \{\Phi | \Phi \varepsilon H,\ \langle\Phi,\theta_n\rangle = 0\} \ . \tag{1.4}$$

Apart from their intrinsic theoretical interest, bounding variational functionals can in principle lead (with suitably artificial choice of trial vector) to bounds on unknown quantities in terms of certain known quantities, like sum rules or moments [4,6]. However, if they are to be a viable practical tool, bounding functionals must not present exceptionally severe problems of evaluation when reasonable trial vectors are employed. It is

for this reason that we do not much concern ourselves with functionals which involve powers of the operator h higher than the second.

2. A BIVARIATIONAL APPROXIMATION TO Z

Variational approaches to the task of bounding Z stem from its alternative but equivalent specification in terms of the solution-vector ϕ of the equation in H_n

$$(h-E_n+\zeta)\phi = f , \qquad \phi,f \in H_n . \tag{2.1}$$

This is simply

$$Z(f,g;\zeta) = 2 \text{ Real } \langle g,\phi\rangle = \langle g,\phi\rangle + \langle \phi,g\rangle . \tag{2.2}$$

Setting $\zeta = \nu + i\omega$ (with ν and ω real), and defining for convenience

$$H = h-E_n+\nu , \tag{2.3}$$

equation (2.1) is

$$A\phi = f , \qquad \phi,f \in H_n \tag{2.4}$$

with

$$A = H + i\omega . \tag{2.5}$$

This decomposition of the linear operator A as the sum of a self-adjoint part H and a skew-self-adjoint part $i\omega$ is important for the establishment of the bounds in §3.

Along with equation (2.4) we consider the auxiliary equation

$$A^*\psi = g , \qquad \psi, g \in H_n \tag{2.6}$$

where

$$A^* = H - i\omega \tag{2.7}$$

is the Hilbert-space adjoint of A. We note that

$$\langle \phi, g \rangle = \langle \phi, A^*\psi \rangle = \langle A\phi, \psi \rangle = \langle f, \psi \rangle , \tag{2.8}$$

so that we can express Z in the form

$$Z(f,g;\zeta) = \langle g, \phi \rangle + \langle f, \psi \rangle \tag{2.9}$$

in terms of the solution-vectors ϕ and ψ of equations (2.4) and (2.6).

Associated with this pair of equations is the bivariational approximation to $\langle g, \phi \rangle$ given by

$$R(\Psi, \Phi) = -\langle \Psi, A\Phi \rangle + \langle \Psi, f \rangle + \langle g, \Phi \rangle , \qquad \Psi, \Phi \in H_n , \tag{2.10}$$

with the trial vector Ψ playing the role of a kind of Lagrange multiplier. In terms of the difference vectors

$$\delta\psi = \Psi - \psi \in H_n, \qquad \delta\phi = \Phi - \phi \in H_n, \tag{2.11}$$

we have the relation

$$R(\Psi,\Phi) = \langle g,\phi\rangle - \langle \delta\psi, A\delta\phi\rangle . \tag{2.12}$$

The complex conjugate of $R(\Psi,\Phi)$ is

$$\bar{R}(\Psi,\Phi) = -\langle\Phi,A^*\Psi\rangle + \langle\Phi,g\rangle + \langle f,\Psi\rangle \tag{2.13}$$

$$= \langle f,\psi\rangle - \langle\delta\phi,A^*\delta\psi\rangle , \tag{2.14}$$

which is a bivariational approximation to $\langle f,\psi\rangle$ (or $\langle\phi,g\rangle$). Thus, by addition, the real functional

$$J(\Psi,\Phi) = R(\Psi,\Phi) + \bar{R}(\Psi,\Phi)$$

$$= -\langle\Psi,A\Phi\rangle - \langle\Phi,A^*\Psi\rangle + \langle\Psi,f\rangle + \langle f,\Psi\rangle + \langle g,\Phi\rangle + \langle\Phi,g\rangle \tag{2.15}$$

is a bivariational approximation to

$$J(\psi,\phi) = \langle g,\phi\rangle + \langle f,\psi\rangle = Z(f,g;\zeta) \tag{2.16}$$

with the property

$$J(\Psi,\Phi) = Z(f,g;\zeta) - \langle\delta\psi,A\delta\phi\rangle - \langle\delta\phi,A^*\delta\psi\rangle . \tag{2.17}$$

3. MIXED VARIATIONAL BOUNDS ON Z

In the event that H (the self-adjoint part of A) is a positive operator, with an inverse H^{-1}, it is possible to construct two special cases of the bivariational functional $J(\Psi,\Phi)$ which provide complementary (upper and lower) variational bounds on $Z(f,g;\zeta)$. To do this, we think in terms of the 'mixed' vectors

$$x = \lambda\phi + \mu\psi \,, \tag{3.1}$$

$$y = \lambda\phi - \mu\psi \,, \tag{3.2}$$

where the scalar multipliers λ and μ are real and satisfy

$$2\lambda\mu = 1 \,. \tag{3.3}$$

Combining equations (2.4) and (2.6), we see that x and y are the solution-vectors of the simultaneous equations

$$Hx + i\omega y = \lambda f + \mu g = p \text{ (say)} \,, \tag{3.4}$$

and

$$Hy + i\omega x = \lambda f - \mu g = q \text{ (say)} \,. \tag{3.5}$$

If we now choose trial vectors

$$X = \lambda\Phi + \mu\Psi \,, \tag{3.6}$$

$$Y = \lambda\Phi - \mu\Psi \,, \tag{3.7}$$

and let

$$\delta x = X - x = \lambda\delta\phi + \mu\delta\psi \,, \tag{3.8}$$

$$\delta y = Y - y = \lambda\delta\phi - \mu\delta\psi \,, \tag{3.9}$$

we find that, using (3.3),

$$J(\Psi,\Phi) = I(X,Y) = -\langle X,HX\rangle + \langle Y,HY\rangle - \langle X,i\omega Y\rangle + \langle Y,i\omega X\rangle + \langle X,p\rangle + \langle p,X\rangle - \langle Y,q\rangle - \langle q,Y\rangle \tag{3.10}$$

and

$$I(X,Y) = Z(f,g;\zeta) - \langle\delta x,(H\delta x + i\omega\delta y)\rangle + \langle\delta y,(H\delta y + i\omega\delta x)\rangle \,. \tag{3.11}$$

Accordingly, if the trial vectors X and Y are constrained to satisfy the equation

$$HX + i\omega Y = p \tag{3.12}$$

in line with (3.4), so that

$$H\delta x + i\omega\delta y = 0 \,, \tag{3.13}$$

it follows that the resulting functional $I_+(X,Y)$ has the property

$$I_+(X,Y) = Z(f,g;\zeta) + \langle\delta y,(H+\omega^2H^{-1})\delta y\rangle \,, \tag{3.14}$$

and is thus a variational upper bound on Z. Similarly, if

$$HY + i\omega X = q \ , \tag{3.15}$$

in line with (3.5), so that

$$H\delta y + i\omega\delta x = 0 \ , \tag{3.16}$$

it follows that the resulting function $I_-(X,Y)$ has the property

$$I_-(X,Y) = Z(f,g;\zeta) - \langle \delta x, (H+\omega^2 H^{-1})\delta x \rangle \ , \tag{3.17}$$

and is thus a variational lower bound on Z .

In terms of an arbitrary trial vector Y , we have

$$I_+(X,Y) = I(H^{-1}(p-i\omega Y),Y) = K_+(Y) \quad \text{say,} \tag{3.18}$$

with

$$K_+(Y) = \langle Y,HY \rangle + \langle (p-i\omega Y), H^{-1}(p-i\omega Y) \rangle - \langle Y,q \rangle - \langle q,Y \rangle \ . \tag{3.19}$$

Similarly,

$$I_-(X,Y) = I(X,H^{-1}(q-i\omega X)) = K_-(X) \quad \text{say,} \tag{3.20}$$

with

$$K_-(X) = -\langle X,HX \rangle - \langle (q-i\omega X), H^{-1}(q-i\omega X) \rangle + \langle X,p \rangle + \langle p,X \rangle \ . \tag{3.21}$$

Thus we obtain the complementary upper and lower variational bounds

$$K_-(X) \leq K_-(x) = Z(f,g;\zeta) = K_+(y) \leq K_+(Y) \ , \tag{3.22}$$

with the bounding functionals each depending on a single 'mixed' complex vector. Hence we call them 'mixed' variational bounds. It is a straightforward matter to optimize the functionals with respect to parameters multiplying the trial vectors, and if H is real there is separation of contributions from the real and imaginary parts of the trial vectors. The ratio $\lambda:\mu$ is also a disposable parameter.

These mixed variational bounds hold good whenever

$$E_0 - E_n + \nu > 0 , \qquad n \neq 0 , \tag{3.23}$$

E_0 being the lowest energy eigenvalue of h. In the case $n = 0$, they hold whenever

$$E_1 - E_0 + \nu > 0 , \tag{3.24}$$

E_1 being the closest eigenvalue to E_0, since H_0 does not contain θ_0. If E_0 is degenerate, then $E_1 = E_0$. Given that (3.23) or (3.24) holds, we have

$$\langle\Phi,(h-E_n+\nu)\Phi\rangle = \langle\Phi,H\Phi\rangle \geq b\langle\Phi,\Phi\rangle , \qquad b > 0 , \tag{3.25}$$

for all $\Phi \in H_n$, with

$$b = E_0 - E_n + \nu,\ n \neq 0; \qquad b = E_1 - E_0 + \nu,\ n = 0 . \tag{3.26}$$

It follows from (3.25) that H is positive, and since it is bounded below away from zero the inverse operator H^{-1} exists with domain the whole of H_n.

The idea of introducing a mixture of equations like (2.4) and (2.6) in order to obtain bounds has been exploited for dissipative systems in real spaces by Collins [13]; see also Herrera [14,15]. The bivariational functional $I(X,Y)$ shows the saddle-type dependence on X and Y which is necessary for complementary bounds [16,17].

4. AVOIDANCE OF H^{-1}; IMPLICIT BIVARIATIONAL BOUNDS

A practical disadvantage of the bounding functionals $K_+(Y)$ and $K_-(X)$ is that they involve the inverse H^{-1}, which only in elementary cases is likely to have a representation simple enough to permit the evaluation of the relevant inner products. One way of avoiding H^{-1} in $K_+(Y)$ is to write K_+ as a functional of X via (3.12) giving

$$K_+(Y(X)) = I(X,\tfrac{i}{\omega}(HX-p)) = \tfrac{1}{\omega^2}\langle(HX-p),H(HX-p)\rangle + \langle X,HX\rangle - \tfrac{i}{\omega}\langle(HX-p),q\rangle + \tfrac{i}{\omega}\langle q,(HX-p)\rangle . \tag{4.1}$$

Similarly,

$$K_-(X(Y)) = I(\tfrac{i}{\omega}(HY-q),Y) = -\tfrac{1}{\omega^2}\langle(HY-q),H(HY-q)\rangle - \langle Y,HY\rangle + \tfrac{i}{\omega}\langle(HY-q),p\rangle - \tfrac{i}{\omega}\langle p,(HY-q)\rangle . \tag{4.2}$$

However, these forms involve H^3 (as well as factors of ω^{-1}), and we rule them out as impractical.

A better way of avoiding the H^{-1} terms in (3.19) and (3.21) is to bound them separately, using individual variational bounds of the type

$$\langle \ell, H^{-1}\ell \rangle \leq -\langle \chi, H\chi \rangle + \langle \chi, \ell \rangle + \langle \ell, \chi \rangle + \frac{1}{b}\|H\chi - \ell\|^2 \ , \quad \ell, \chi \in H_n, \ b > 0 \ , \tag{4.3}$$

which follow from the positivity hypothesis (3.25). Taking $\ell = p - i\omega Y$ and $\chi = \tilde{X}$ in (4.3), we find that (3.19) gives, after simplification,

$$K_+(Y) \leq I(\tilde{X}, Y) + \frac{1}{b}\|H\tilde{X} + i\omega Y - p\|^2 \ . \tag{4.4}$$

Similarly, putting $\ell = q - i\omega X$ and $\chi = \tilde{Y}$ in (4.3), we obtain from (3.21) the result

$$K_-(X) \geq I(X, \tilde{Y}) - \frac{1}{b}\|H\tilde{Y} + i\omega X - q\|^2 \ . \tag{4.5}$$

Dropping the tildes in (4.4) and (4.5), we see from (3.22) that for arbitrary vectors X and Y in H_n,

$$I(X,Y) - \frac{1}{b}\|HY + i\omega X - q\|^2 \leq Z(f,g;\zeta) \leq I(X,Y) + \frac{1}{b}\|HX + i\omega Y - p\|^2 \ . \tag{4.6}$$

These are <u>bivariational</u> bounds on $Z(f,g;\zeta)$, which with prescience we might have derived directly from (3.11) and (3.25). They hold whenever H is positive and bounded below away from zero, so that a suitable positive b can be found according to (3.26).

The mixed vectors (x,y) and (X,Y) were introduced with the object of deriving variational bounds depending on a single trial vector, and so their usefulness has evaporated in (4.6). Referring back to the original vectors (ψ,ϕ) and (Ψ,Φ), the bivariational bounds (4.6) become

$$J(\Psi,\Phi) - \frac{1}{b}\{\lambda^2\|A\Phi-f\|^2+\mu^2\|A^*\Psi-g\|^2 - \mathrm{Re}\langle A\Phi-f,A^*\Psi-g\rangle\} \le Z(f,g;\zeta) \le J(\Psi,\Phi) + \frac{1}{b}\{\lambda^2\|A\Phi-f\|^2+\mu^2\|A^*\Psi-g\|^2 + \mathrm{Re}\langle A\Phi-f,A^*\Psi-g\rangle\} . \tag{4.7}$$

With the optimal choice for the ratio $\lambda:\mu$ of

$$\lambda\|A\Phi-f\| = \mu\|A^*\Psi-g\| , \qquad (2\lambda\mu = 1) , \tag{4.8}$$

we obtain the result

$$\boxed{J(\Psi,\Phi) + \frac{1}{b}S(\Psi,\Phi) - \frac{1}{b}C(\Psi,\Phi) \le Z(f,g;\zeta) \le J(\Psi,\Phi) + \frac{1}{b}S(\Psi,\Phi) + \frac{1}{b}C(\Psi,\Phi)} , \tag{4.9}$$

where, in terms of H,

$$J(\Psi,\Phi) = -\langle\Psi,H\Phi\rangle - \langle\Phi,H\Psi\rangle + i\omega\{\langle\Phi,\Psi\rangle - \langle\Psi,\Phi\rangle\} + \langle\Psi,f\rangle + \langle f,\Psi\rangle + \langle g,\Phi\rangle + \langle\Phi,g\rangle , \tag{4.10}$$

$$S(\Psi,\Phi) = \mathrm{Real}\,\langle(H+i\omega)\Phi-f,(H-i\omega)\Psi-g\rangle = \mathrm{Real}\,\langle A\delta\phi,A^*\delta\psi\rangle , \tag{4.11}$$

and

$$C(\Psi,\Phi) = \|(H+i\omega)\Phi-f\|\,\|(H-i\omega)\Psi-g\| = \|A\delta\phi\|\,\|A^*\delta\psi\| . \tag{4.12}$$

We call the bivariational bounds (4.9) implicit, because they are contained in the mixed bounds (3.22).

In the special case of zero ω, when A becomes self-adjoint, the implicit bounds (4.9) are actually tighter than others previously derived for self-adjoint operators in real spaces [18, see also 19].

5. EXPLICIT BIVARIATIONAL BOUNDS

The bounds in (4.9) only hold when the operator H is positive and bounded below away from zero by a positive b, given by (3.26). However, irrespectively of whether this condition is met, it is possible to derive explicitly alternative bivariational bounds which merely require the condition

$$||A\Phi|| \geq a||\Phi|| , \quad a > 0 , \qquad \text{for all } \Phi \in H_n . \tag{5.1}$$

Since

$$\begin{aligned} ||A\Phi||^2 &= \langle A\Phi, A\Phi\rangle = \langle \Phi, A^*A\Phi\rangle = \langle \Phi, H^2\Phi\rangle + \omega^2\langle\Phi,\Phi\rangle \\ &\geq (E_{n'}-E_n+\nu)^2 \, ||\Phi||^2 + \omega^2 \, ||\Phi||^2, \end{aligned} \tag{5.2}$$

where $E_{n'}$ is the energy eigenvalue of h which minimizes $(E_{n'}-E_n+\nu)^2$, we see that condition (5.1) is satisfied by taking

$$a^2 = (E_{n'}-E_n+\nu)^2 + \omega^2 , \qquad a > 0 . \tag{5.3}$$

We bear in mind that $E_{n'} \neq E_n$ (unless E_n is degenerate), since H_n does not contain θ_n. Thus, disregarding the exceptional case of zero ζ and degenerate E_n, we can always find a constant a to satisfy (5.1).

Applying (5.1) to (4.12), and then using Schwarz's inequality, we have

$$C(\Psi,\Phi) \geq a\|\delta\phi\| \, \|A\delta\psi\| \geq a|\langle\delta\phi, A^*\delta\psi\rangle| \, . \tag{5.4}$$

The magnitude of the complex number on the right of (5.4) is greater than or equal to the magnitude of its real part, and so from (2.17) it follows that

$$C(\Psi,\Phi) \geq \tfrac{1}{2}a|\langle\delta\phi, A^*\delta\psi\rangle + \langle\delta\psi, A\delta\phi\rangle| = \tfrac{1}{2}a|Z-J(\Psi,\Phi)| \, . \tag{5.5}$$

Rearranging (5.5) we obtain at once the explicit bivariational bounds

$$\boxed{J(\Psi,\Phi) - \frac{2}{a}C(\Psi,\Phi) \leq Z(f,g;\zeta) \leq J(\Psi,\Phi) + \frac{2}{a}C(\Psi,\Phi)} \, . \tag{5.6}$$

Existence theorems for bounds of this type have recently been presented, together with some applications [20,21].

6. THE CASE $f = g$

When $f = g$, as is the case for the dynamic polarizability $\alpha(\zeta)$ in (1.1), the equations (2.4) and (2.6) become

$$(H+i\omega)\phi = f = (H-i\omega)\psi \, . \tag{6.1}$$

If a similar relationship is imposed on the trial vectors Ψ and Φ by taking

$$\Phi = (H-i\omega)\Theta, \qquad \Psi = (H+i\omega)\Theta , \tag{6.2}$$

for some trial vector Θ which is supposed to approximate $(H^2+\omega^2)^{-1}f$, the functionals in (4.9) and (5.6) become

$$J = -2\langle\Theta,H(H^2+\omega^2)\Theta\rangle + 2\langle f,H\Theta\rangle + 2\langle H\Theta,f\rangle , \tag{6.3}$$

and

$$C = S = \|(H^2+\omega^2)\Theta-f\|^2 . \tag{6.4}$$

The bivariational bounds (4.9) and (5.6) become variational bounds, involving high powers of H , of a type previously obtained [3,5]. The H^3 and H^4 rule them out for practical purposes. Thus there seems little point in trying to impose a constraint like (6.2). However, when choosing trial vectors, it would be sensible to have in mind the relationship between the respective ω-dependence of Φ and Ψ which is implied by (6.2).

There are some simplifications to be made if f is a real vector, and the Hamiltonian h (and hence H) is a real operator. Then it follows from (6.1) that $\psi = \bar{\phi}$. Accordingly, let us set

$$\Phi = \Phi_1 + i\Phi_2, \qquad \Psi = \Phi_1 - i\Phi_2 = \bar{\Phi} , \tag{6.5}$$

in the functionals J, C and S, where Φ_1 and Φ_2 are real vectors. We obtain the functionals

$$J(\bar{\Phi},\Phi) = -2\langle\Phi_1,H\Phi_1\rangle + 2\langle\Phi_2,H\Phi_2\rangle + 4\omega\langle\Phi_1,\Phi_2\rangle + 4\langle\Phi_1,f\rangle , \tag{6.6}$$

$$C(\bar{\Phi},\Phi) = \|H\Phi_1-\omega\Phi_2-f\|^2 + \|H\Phi_2+\omega\Phi_1\|^2 , \tag{6.7}$$

and

$$S(\bar{\Phi},\Phi) = \|H\Phi_1-\omega\Phi_2-f\|^2 - \|H\Phi_2+\omega\Phi_1\|^2 . \tag{6.8}$$

The implicit bivariational bounds (4.9) become

$$J(\bar{\Phi},\Phi) - \frac{2}{b}\|H\Phi_2+\omega\Phi_1\|^2 \le Z(f,f;\zeta) \le J(\bar{\Phi},\Phi) + \frac{2}{b}\|H\Phi_1-\omega\Phi_2-f\|^2 , \tag{6.9}$$

and the explicit bounds (5.6) take the form

$$J(\bar{\Phi},\Phi) - \frac{2}{a}C(\bar{\Phi},\Phi) \le Z(f,f;\zeta) \le J(\bar{\Phi},\Phi) + \frac{2}{a}C(\bar{\Phi},\Phi) \tag{6.10}$$

which at $\nu = 0$ is essentially that given by Burrows [8]. The mixed bounds $K_+(Y)$ and $K_-(X)$ simplify in this situation, too, particularly if we take $\lambda = \mu = 2^{-1/2}$, so that $X = \Phi_1\sqrt{2}$, $Y = i\Phi_2\sqrt{2}$, $p = f\sqrt{2}$ and $q = 0$, yielding

$$K_+(Y) = 2\langle\Phi_2,H\Phi_2\rangle + 2\langle(f+\omega\Phi_2),H^{-1}(f+\omega\Phi_2)\rangle \tag{6.11}$$

and

$$K_-(X) = -2\langle\Phi_1,H\Phi_1\rangle - 2\omega^2\langle\Phi_1,H^{-1}\Phi_1\rangle + 4\langle\Phi_1,f\rangle . \tag{6.12}$$

Goscinski [4] has given the amplitude-optimized version of the bound in (6.12) for $\nu = 0$.

7. DISCUSSION

Interest in the mixed variational bounds $K_+(Y)$ and $K_-(X)$ is primarily theoretical. Not only do they contain the implicit bivariational bounds, but also they can lead to bounds in terms of other known quantities. To take a simple example, when ω is small the solution to equation (2.4) is approximately $H^{-1}f - i\omega H^{-2} f$. Thus if we take

$$\Phi_1 = c_1 H^{-1} f, \qquad \Phi_2 = -i\omega c_2 H^{-2} f \tag{7.1}$$

in the simplified functionals (6.11) and (6.12), and optimize with respect to c_1 and c_2, we should obtain bounds on $Z(f,f;\zeta)$ which are accurate for small ω . The bounds are

$$s_{-2} - \omega^2\left(\frac{1}{s_{-4}} + \frac{\omega^2}{s_{-2}}\right)^{-1} \leq \tfrac{1}{2}Z(f,f;\zeta) \leq s_{-2} - \omega^2\left(\frac{1}{s_{-4}} + \frac{\omega^2 s_{-6}}{(s_{-4})^2}\right)^{-1} \tag{7.2}$$

in terms of the 'sum rules'

$$s_n = \langle f, H^{n+1} f \rangle . \tag{7.3}$$

For ground-state hydrogen, the bounds (7.2) give the result (in atomic units)

$$4.2490 \leq \alpha(i\omega) \leq 4.2503 \tag{7.4}$$

for the dipole polarizability at $\nu = 0$, $\omega = 0.1$.

When H is positive the quantity $Z(f,f;\zeta)$ is a series-of-Stieltjes-representable function of ω^2, and with suitable choices of trial vector different families of Padé approximant bounds can be derived from K_+ and K_- [6,22]. More generally, whenever $\langle f,(H^2+\omega^2)^{-1}g\rangle$ is real, it can be shown that

$$Z(f,g;\zeta) = \langle(H^{1/2}p),(H^2+\omega^2)^{-1}(H^{1/2}p)\rangle - \langle(H^{1/2}q),(H^2+\omega^2)^{-1}(H^{1/2}q)\rangle \ , \quad (7.5)$$

whence $Z(f,g;\zeta)$ is the difference of two series-of-Stieltjes-representable functions. The K_+ and K_- functionals are again the appropriate ones to yield the Padé approximant bounds for this kind of situation [23], rather than bivariational functionals which lead to Padé approximants plus correction terms [21,24].

From a practical standpoint, it is unlikely that a convenient representation of H^{-1} will be available, in which case the mixed bounds $K_+(Y)$ and $K_-(X)$ are not of direct interest even though they only involve a single trial vector. Likewise bounding functionals containing H^3 and higher powers can be ignored, because of the consequent difficulties in evaluating the inner products when sensible trial vectors are employed. Thus for a practical tool we are left with the bivariational bounds, in either the implicit form (4.9) (only valid when H is bounded below away from zero by a positive number b) or the explicit form (5.6) (always valid). Although an extra trial vector is involved, only H and H^2 appear in the inner products and this advantage is crucial. The bivariational bounds should still be used even when $f = g$; the simpler versions (6.9) or (6.10) are relevant when $f = g$ is a real vector and H is real.

Even when the implicit bounds (4.9) are available, they will not necessarily yield better results than the explicit bounds (5.6). For example, when ω is large, the number a (given by (5.3)) is of order ω, whereas the number b (given by (3.26)) is not. With the correct asymptotic choices

$$\Phi = \frac{-if}{\omega}, \qquad \Psi = \frac{ig}{\omega} \tag{7.6}$$

the explicit bounds give

$$J \pm \frac{2}{a} C = \frac{i}{\omega}(\langle f,g\rangle - \langle g,f\rangle) + \frac{1}{\omega^2}(\langle f,Hg\rangle + \langle g,Hf\rangle) \pm O(\frac{1}{\omega^3}), \tag{7.7}$$

whereas the bounds (4.9) leave some uncertainty in the ω^{-2} term. However, in cases like (6.4) when (S-C) is zero, or very small, it is clear that the lower bound in (4.9) is better than the lower bound in (5.6). We notice also that the explicit bounds can never have quite the correct ω-dependence because of the square-root defining the number a. Thus, when both are available, the implicit and the explicit bivariational bounds should each be investigated in any given situation to see which gives the better results.

Extensive calculations of bounds on dynamic polarizabilities (f=g) for two-electron atoms at zero ω or zero ν have recently been carried out by Glover and Weinhold [25-27]. The functionals of Braun and Rebane [2] which they employed led to inaccuracies for small values of ω. Applications of the Glover-Weinhold techniques to the bivariational bounds developed here are being explored. A pleasing feature of the present approach is that the same bivariational functionals provide bounds whether or not ω=0, ν=0, or f=g.

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New variational bounds are derived on the generalized polarizabilities of a quantum-mechanical system, for arbitrary complex frequencies $\zeta=\nu+i\omega$ and two different perturbations u and v. No power of the Hamiltonian h higher than h^2 is involved in the bounding functionals. For a certain range of ν-values, upper and lower bounding functionals are obtained which contain merely a single trial vector but also introduce an inverse operator like h^{-1}. This impractical feature can be avoided with a subsidiary variational principle, leading to bivariational upper and lower bounds. Explicit bivariational bounds are also derived which are valid for all values of ζ. Both theoretical and practical aspects of the bounds are discussed.

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